COMPORTEMENT DES MEMBRANES/PÉTROLE BRUT DANS LA FILTRATION D'ÉMULSIONS DILUÉES DE PÉTROLE BRUT/EAU

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MEMBRANE/CRUDE OIL BEHAVIOUR IN DILUTE CRUDE OIL/WATER EMULSION FILTRATION

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RÉSUMÉ

Les émulsions de pétrole brut sont souvent présentes dans les différentes opérations de l'industrie pétrolière. Dans la production de pétrole brut, après les traitements préalables pour la séparation Pétrole/Eau, au moyen par exemple de séparateurs API, on obtient des émulsions de pétrole brut dans l'eau très diluées. Ces émulsions doivent dans de nombreux cas faire l'objet de nouveaux traitements, si une réutilisation de l'eau est prévue ou si ces émulsions doivent être rejetées dans l'environnement. La filtration sur membrane, qui permet de séparer l'eau des petites gouttelettes de pétrole, est l'un des processus pouvant être utilisé pour ce type de traitement. Nous avons utilisé dans ces recherches différentes membranes organiques pour filtrer des émulsions de pétrole brut dilué dans l'eau et avons étudié leur comportement. Trois types différents de pétrole brut ont été utilisés : léger, moyen et lourd avec des gravités API de 33,4°, 24,6° et 13,8°. Des mesures de potentiel Zêta, d'angle de contact et de tension interfaciale ont été effectuées. Les résultats des expériences de filtration montrent que lorsque la membrane est plus hydrophobe, l'adsorption de pétrole brut est plus importante et par conséquent l'encrassement des membranes est lui aussi plus important. Ces données viennent confirmer les mesures d'angle de contact qui indiquent qu'à mesure que le mouillage de la membrane avec le pétrole augmente, l'encrassement augmente également. De même, lorsque les conditions physico-chimiques sont modifiées, comme le pH par exemple, les conditions de mouillage du pétrole brut changent et l'encrassement peut être réduit.

ABSTRACT

Crude oil emulsions are often found in different operations of the oil industry. In crude oil production, after previous treatments for Oil/Water separation, like in API separators, very dilute crude oil in water emulsions are obtained. These emulsions should, in many cases, be further treated if water is to be reused or if it disposed into the environment. One of the processes that could be used for this treatment is membrane filtration, were water can be separated from the small oil droplets. In this work, different organic membranes were used to filter dilute crude oil in water emulsions and their behaviour studied. Three different types of crude oil were used: light, medium and heavy with API gravities of 33,4°, 24,6° and 13,8°. Zeta potential, contact angle and interfacial tension measurements were made. Results of the filtration experiments show that when the membrane is more hydrophobic, there is more adsorption of crude oil and thus more membrane fouling. This agrees with the contact angle measurements that show that as wetting of the membrane with oil increases, the fouling also increases. Also, when physicochemical conditions are changed, as pH for example, the wetting of the crude oil conditions change and fouling can be reduced.

Mots clés : Emulsion de pétrole brut, Filtration sur membrane, Comportement interfacial

Key words: *Crude Oil Emulsion, Membrane Filtration, Interfacial Behaviour*

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Catégories / *Categories*

-4 New challenges. New ambitions.
4.1 Emulsions and sustainable development

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Abstract

Crude oil emulsions are often found in different operations of the oil industry. In crude oil production, after previous treatments for oil/water separation, like in API separators, very dilute crude oil in water emulsions are obtained. These emulsions should, in many cases, be further treated if reuse of water is to be made or if they are to be disposed into the environment. One of the processes that could be used for this treatment is membrane filtration, wherein water can be separated from the small oil droplets. In this work, different organic membranes were used to filter dilute crude oil in water emulsions and their behaviour studied. Three different types of crude oil were used: light, medium and heavy with API gravities of 33.4°, 24.6° and 13.8°. Zeta potential, contact angle and interfacial tension measurements were made. Results of the filtration experiments show that when the membrane is more hydrophobic, there is more adsorption of crude oil and thus more membrane fouling. This agrees with the contact angle measurements that show that as wetting of the membrane with oil increases, the fouling also increases. Also, when physicochemical conditions are changed, as pH for example, the wetting of the crude oil conditions change and fouling can be reduced.

Keywords: crude oil emulsion, membrane filtration, interfacial behaviour.

Résumé

Des émulsions de pétrole sont souvent trouvées en différentes opérations de l'industrie pétrolière. Dans la production du brut, après avoir séparé l'eau et l'huile avec des séparateurs API, des émulsions très diluées du pétrole dans l'eau sont obtenues. Ces émulsions doivent être traitées, si elles sont utilisées dans d'autres opérations ou jetées dans l'environnement. Un des procédés qui peut être utilisé pour ce traitement est la filtration avec des membranes, où l'eau est séparée des petites gouttes de pétrole. Dans ce travail, des différentes membranes organiques ont été utilisées pour filtrer les émulsions diluées et leur comportement a été étudié. Trois types de pétrole on été utilisés : léger, moyen et lourd, avec des gravités API de : 33,4°, 24,6° et 13,8°. Le potentiel zeta, l'angle de contacte et la tension interfacielle ont été mesurés. Les résultats des filtrations montrent que quand la membrane est hydrophobe, il y a plus d'adsorption du pétrole et plus de colmatage. Les mesures de l'angle de contacte démontrent que quand le mouillage de la membrane avec le pétrole augmente, le colmatage s'incrémente aussi. Également, quand les conditions physicochimiques changent, comme le pH, le mouillage de la membrane par le pétrole change, et le colmatage peut être réduit.

Mots clé : émulsion du pétrole, filtration avec membranes, comportement interfaciel.

1- Introduction

When crude oil is produced, it often comes with some water and sediments. In some cases, the quantity of water produced exceeds that of oil; as for example, some oilfields in Barinas, Venezuela, where the production of one oil barrel comes with eight barrels of water (brine). The oil obtained from the well must be separated from the water (and sediments) and some unit operations are used for this task: separation by gravity in tanks, API separators, air flotation, etc. The quality of the water obtained does not always meet environmental regulations or can be reused in other operations in the oilfields. The water obtained after conventional separation may contain little quantities of oil forming very dilute O/W emulsions. One operation suited to treat these dilute O/W emulsions is membrane filtration. Very diluted emulsions between 20 and 100 ppm of oil have been treated by micro-filtration and ultra-filtration membranes obtaining concentrations of less than 3 ppm of oil, below the environmental regulations limit of 5 ppm (1). One problem associated with membrane treatment is fouling, which reduces the membrane capacity, and if this fouling is severe, the process becomes unfeasible. Fouling is related to the adhesion of particles (or viscous fluids) to the membrane surface or membrane pores. Thus, the interaction between the membrane (solid) and the oil and water is of utmost importance in membrane behaviour. The wetting characteristics of the membrane are very important in its fouling tendency, and to obtain water and concentrate the oil emulsion, a membrane that does not wet by crude oil is desirable. In certain way, the idea is to have a hydrophilic membrane where the oil does not attach to it (fouling it) and this parallels the behaviour of oil and water (brine) in rock reservoirs, where to displace oil from the rock, the rock must be water wetted (2-3). The work of adhesion of the oil on the solid phase (membrane) is given by the following equation:

$$W_{OM}=\gamma_{OW}(1-\cos\theta)$$

Where θ is the contact angle with respect to water, γ_{OW} is the interfacial energy between the oil-water interface and W_{OM} is the work of adhesion between the solid (membrane) and the oil phase. When the contact angle between the oil phase and the membrane is 180° (0° contact angle for water) there is no adhesion of the oil on the surface of the membrane. Studies have shown that fouling is often related to the organic materials that adhere to the membranes (4), and thus, a way to reduce fouling is to use hydrophilic surfaces. Also, the characteristics of the membrane and emulsion droplet surface can change if the physicochemical environment changes, leading to changes in the wetting behaviour of the fluids involved in the filtration, and these changes can influence in an important way the behaviour of the membrane in the filtration.

In this work, three different types of crude oil and different types of membranes (hydrophobic and hydrophilic) were tested to observe the membrane behaviour towards each type of crude oil and the its physicochemical environment.

2- Experimental

Three types of Venezuelan crude oils were used in this study: light crude (Apure), medium crude (Rosa) and heavy crude (Pilón). Their characteristics are shown in table 1.

Table1. Characteristics of different types of Venezuelan crude oils studied

Type	Apure	Rosa	Pilón
API gravity	33.4°	24.6°	13.8°
K_{uop}	12	13	11.78
Crude nature	Mixed	Paraffinic	Naphthenic
Neutralization number (mg KOH/g)	0.154	0.32	3.0
Asphaltene content	1.58%	2.5%	11.5%

K_{uop} is the characterization factor related to the crude nature

Table 1 shows that the crude oils are of very different characteristics, being the heavier the one with the highest acid number and asphaltene content.

As dispersant sodium pyrophosphate decahydrate (Riedel de Haen, analytical grade) was used. Distilled water was used in all the experiments.

The membranes used were regenerated cellulose (Millipore), polysulphone (Millipore) and polyvinylidene fluoride/ polyvynilpirrolidone, PVDF/PVP (Universidad San Luis, Argentina).

The contact angle was measured using a Rame Hart 100 goniometer with a 40x microscope and a dosing syringe Gillmont of 2 ml. The drops measured where of approximately 40 μL. A special glass cell was constructed to support the membrane and the saline (sodium pyrophosphate decahydrate) solution used. The measurements were made each five minutes for the first 20 minutes and then each 20 minutes until equilibrium was reached (between 180 and 240 minutes). The sodium pyrophosphate decahydrate saline solutions were in concentrations of 0, 0.1%, 0.5%, 1% and 5%.

The interfacial tension between the aqueous solution and the crude oil was measured with a Du Nuoy ring on a Fisher Scientific Tensiomat 21 model. For very low interfacial tensions, a spinning drop tensiometer constructed by the University of Texas was used. The aqueous phase consisted of saline solutions of sodium pyrophosphate decahydrate in the same concentrations as mentioned above.

The zeta potential of the oil droplets was measured using a Delsa Coulter 440 zetameter.

A Minitan S from Millipore was used for the tangential filtrations of the emulsions which contained sodium pyrophosphate in the aqueous phase. The membrane area was of 30 cm^2. The membranes used were the same type of membranes where the contact angles were measured.

3- Results and discussion

The interfacial tension between the aqueous solutions of sodium pyrophosphate and the different crude oils was measured. A change in the interfacial tension for all the crude oils was observed (figure 1), and as the concentration of sodium pyrophosphate increased, the interfacial tension between the aqueous phase and the oil phase decreased. The pyrophosphate is used as a dispersant, to diminish the coalescence of the emulsion and its tendency to stick to the walls of the filtration equipment. But the sodium pyrophosphate also changes the pH of the aqueous solution; from around 6,5 of pure water to around 10 at a concentration of 0.5 %, when, above this concentration there is no further change in the pH value. The pH change brings a change in the behaviour of different kinds of molecules of the crude oil like nafthenic acids, asphaltenes and resins, which tend to activate their surface active properties.

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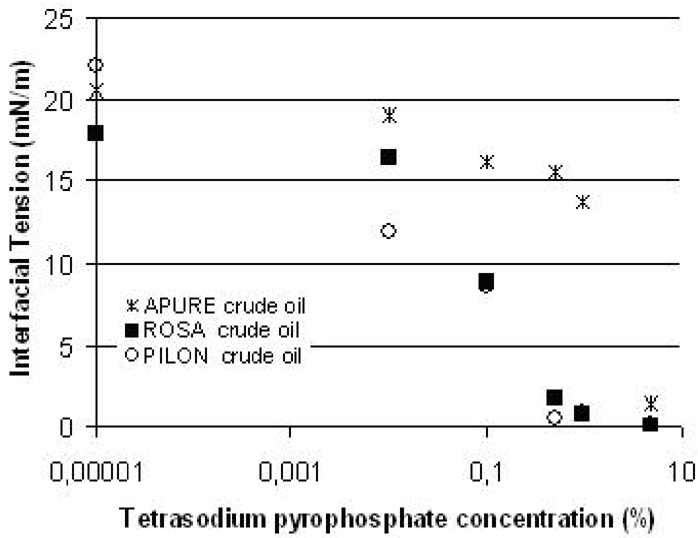

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Figure1. Interfacial tension vs sodium pyrophosphate concentration for the crude oils studied.

Of the three crudes, the lighter crude has a lower interfacial activity if compared with the other two. The Apure light crude has less asphaltenes, resins and less acids (lower neutralization number), which are compounds that tend to have interfacial activity. The other two crudes behave similarly, although the heaviest (Pilón) has far more asphaltenes and a higher neutralization number than the medium gravity crude (Rosa). Some authors point out that for acids in crude oils (5) that not only the quantity of surface active compounds is important, but also its structure. In this study, due to the paraffinic nature of the Rosa crude, the interfacial activity seems to be mostly related to the type of asphaltenes and resins present in this crude oil.

The zeta potential of the different crude oils was measured and the results are shown in figure 2.

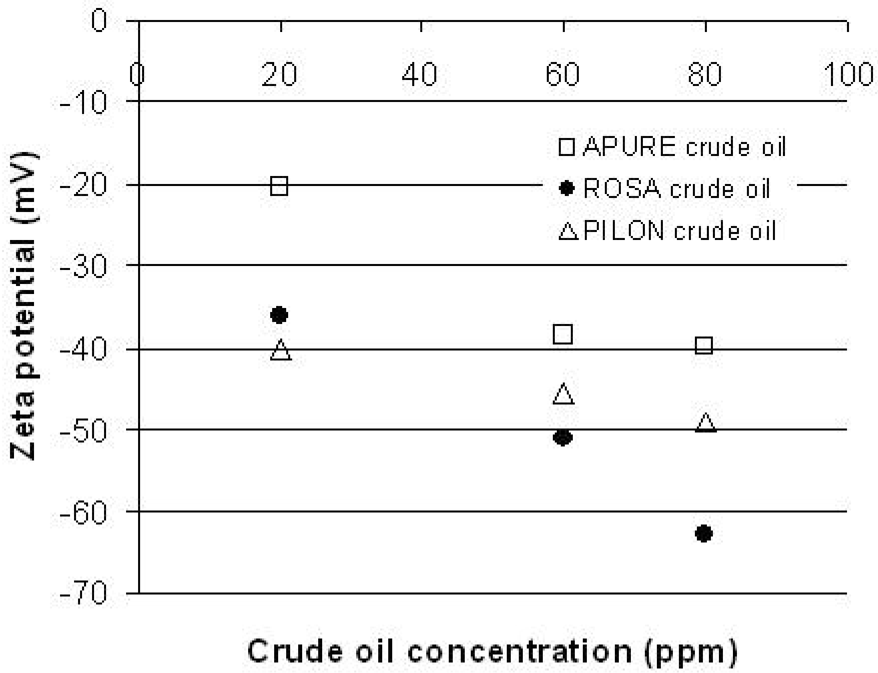

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Figure 2. Zeta potential of different crude oils at different concentrations.

The zeta potential is always negative and increases when the crude oil concentration increases. This is because, as the concentration of the crude oil increases, also the quantity of sodium pyrophosphate is increased. The negative values could be due to the activation of groups with negative charge, like carboxylic acids in a basic environment. Also studies have shown that polysulphone membranes show a negative charge when the pH tends to be basic (6, 7, 8). A similar behaviour is obtained with the regenerated cellulose membranes and with the modified PVDF- PVP membranes. Thus, as the pH becomes more basic, there is an increase in negative charge of the membranes and of the oil droplets which enhances the repulsion of the droplets by the membranes, diminishing the oil wettability of the membranes.

The contact angle measurements show that for the polysulphone membranes, there is a decrease in the wettability of the oil on the membrane as the pH increases. This can be attributed to the changes in surface charge on the droplets and on the membrane. Figure 3 shows the equilibrium contact angles for the polysulphone membrane.

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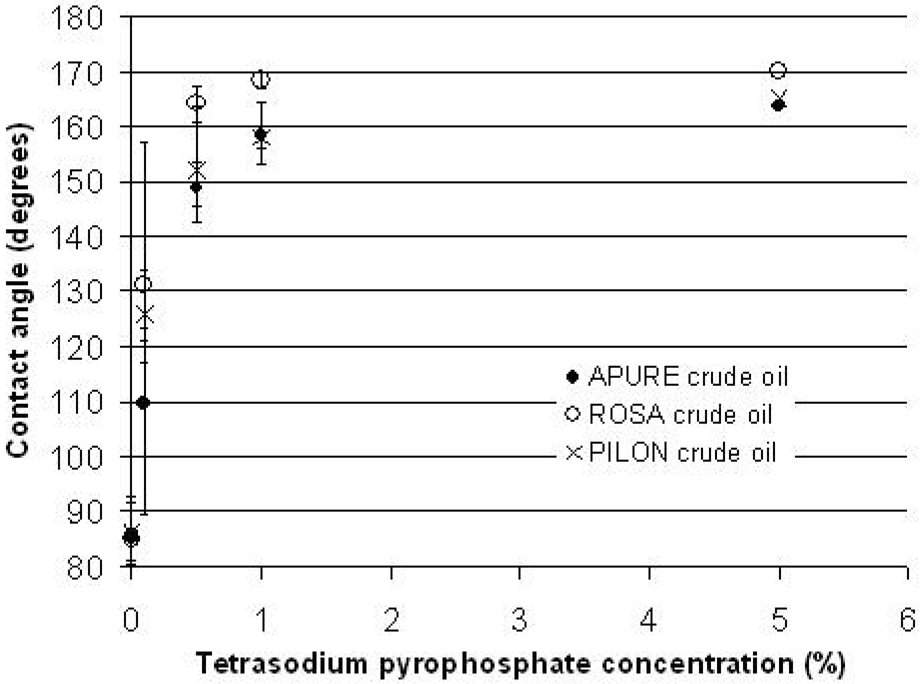

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Figure 3. Equilibrium contact angles for the polysulphone membrane for three types of oil droplets.

The regenerated cellulose membrane tends to be more hydrophilic, even at pH of 6,5 and the measured contact angles were always higher than 160°, reaching values of 168°. This results show that the crude oil does not wet the regenerated cellulose membrane (the adhesion work calculated was less than 1 J/m^2 for the three crude oils studied, while values in the order of 20 J/m^2 were calculated for the polysulphone membrane). The PVDF/PVP membrane modified with polivinipirrolidone (more hydrophilic) also showed higher contact angles (higher than 160°) than the poysulphone membrane alone.

Results show that the wetting properties can change as the physicochemical environment of the system changes; this is more notorious in the polysulphone membrane in which the changes in contact angle (wettability) with pH are relatively important as shown in figure 3. For the other membranes these changes are much smaller. In any case, as the wettability by the oil droplets diminishes, the membrane fouling is expected to diminish also, because the adhesion forces decrease and the oil droplets do not stick to the membrane avoiding plugging the membrane pores.

Filtration experiments were made and it was found that the most hydrophilic membrane (regenerated cellulose) was the one with highest flow of permeate, while the one with the lowest flow of permeate was the polysulphone membrane, the least hydrophilic of all the membranes. It should be stressed that both membranes, regenerated cellulose and polysulphone, had the same cutoff of 100.000 Daltons; the comparison is for membranes with very similar pore diameters. In figure 4 the behaviour of these membranes is shown.

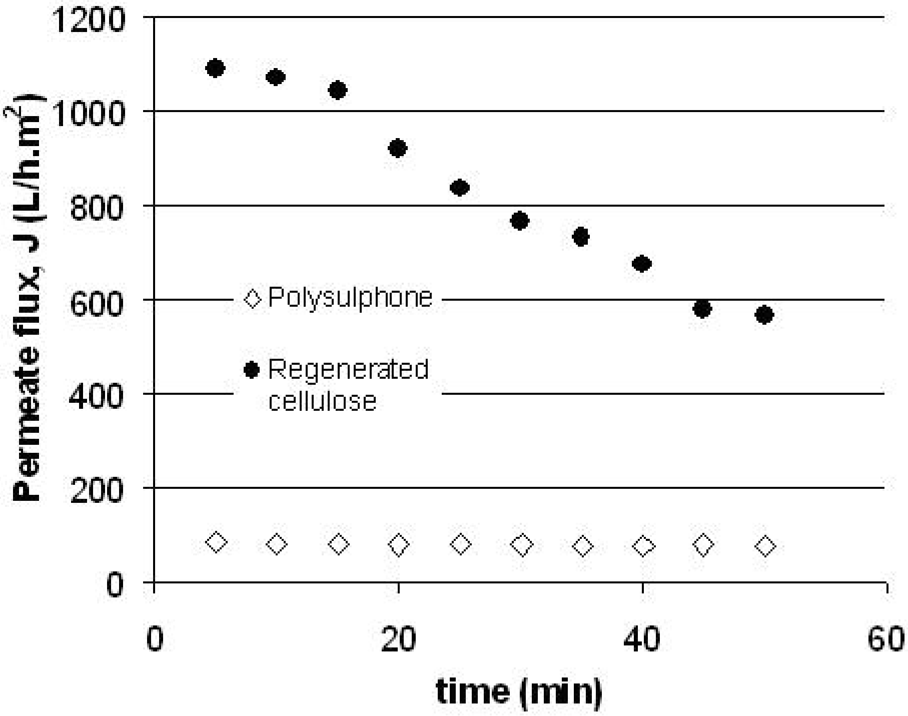

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Figure 4. Permeate flux as a function of time for regenerated cellulose and polysulphone membranes. Crude oil is light Apure.

A high flow of permeate is observed with the regenerated cellulose membrane, which diminishes in time until it tends to reach a constant flow. The polysulphone membrane has a much lower permeate flow, about six times less than the regenerated cellulose membrane when compared at 50 minutes. This results show that the most hydrophilic membrane has a higher permeate flow, even if it diminishes nearly to half of the initial flow (an important part of it can be attributed to hydration of the membrane and not only fouling), than the flow of the polysulphone membrane which is much smaller due to its less hydrophilic character and the possibility of higher fouling. In any case, in these experiments a severe fouling is not expected due to the low concentration of crude oil in water (20 ppm).

4- Conclusions

The variation of the pH brings an important change in the interfacial activity of the three types of crude oils studied. This change in interfacial activity affects the behaviour of the crude oil droplets respect the adhesion to the membranes. As the membranes become more hydrophilic, because of the type of membrane and/or changes in the physicochemical environment, the fouling is decreased.

5- Acknowledgements

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